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(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Manufacture of Alkene Oxide

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Abstract:

A process for the epoxidation of alkene to form alkene oxide comprising contacting alkene and an oxygen-containing gas under epoxidation conditions in the presence of at least one gaseous efficiency-enhancing member of a redox-half reaction pair, e.g., nitric oxide, and a supported silver catalyst containing an efficiency-enhancing amount of a salt of a member of a redox-half reaction pair, e.g., potassium nitrate, drawing from the reaction zone a reactor effluent comprising alkene oxide, carbon dioxide and unreacted alkene, removing at least a portion of the alkene oxide contained in the reactor effluent; recycling at least a portion of the reactor effluent from which the alkene oxide has been removed to the reaction zone after removing sufficient carbon dioxide from the recycle stream to diminish the activity-reducing effect of carbon dioxide.

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IMPROVED PROCESS FOR THE
MANUFACTURE OF ALKENE OXIDE

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Technical Field:

The present invention is directed to improved processes for the preparation of alkene oxide from
15 alkene and oxygen-containing gas employing a supported silver catalyst. Particular aspects of the present invention relate to processes for epoxidizing alkene in the vapor phase to produce the corresponding alkene oxide at high efficiencies.

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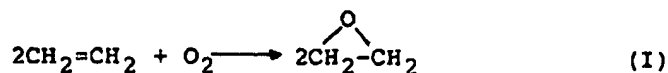
Background And Background Art:

The production of alkene oxides, or epoxides, particularly ethylene oxide, by the direct epoxidation of the corresponding alkene in the presence of a
25 silver-containing catalyst has been known for many years. One of the earliest disclosures of a process for the direct epoxidation of ethylene was that of Lefort, U. S. Patent 1,998,878, issued in 1935 (re-
30 issued in 1942 as Re. 20,370). Lefort discloses that ethylene oxide can be formed by reacting ethylene and oxygen according to the following equation:

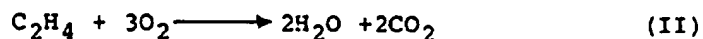
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Lefort recognized, however, that some of the
5 ethylene, when reacted with oxygen, is completely
oxidized to carbon dioxide according to the following
equation:



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Reaction II, as well as other reactions in which
alkene is converted to products other than alkene
oxide, is undesirable since the alkene reactant is
consumed in the formation of undesired products.
15 Further, the undesired products, e.g., carbon di-
oxide, may adversely affect the reaction system. In
general, the overall effectiveness of an alkene oxide
production system is gauged by the performance char-
acteristics of the system. The most important per-
20 formance characteristics are the efficiency, the
activity, and the useful life of the catalyst, all of
which are defined and more completely described be-
low.

Percent conversion is defined as the percentage
25 of the alkene introduced to the reaction system that
undergoes reaction. Of the alkene that reacts, the
percentage that is converted into the corresponding
alkene oxide is referred to as the selectivity or
efficiency of the process. The commercial success of
30 a reaction system depends in large measure on the
efficiency of the system. At present, maximum effi-
ciencies in commercial production of ethylene oxide
by epoxidation are in the low 80s, e.g., 80 or 81
percent. Even a very small increase in efficiency
35 will provide substantial cost benefits in large-scale

operation. For example, taking 100,000 metric tons as a typical yearly yield for a conventional ethylene oxide plant, an increase in efficiency of from 80 to 84 percent, all other things being equal, would result in a savings of 3790 metric tons of ethylene per year. In addition, the heat of reaction for Reaction II (formation of carbon dioxide) is much greater than that of Reaction I (formation of ethylene oxide) so heat-removal problems are more burdensome as the efficiency decreases. Furthermore, as the efficiency decreases, there is the potential for a greater amount of impurities to be present in the reactor effluent which can complicate separation of the desired alkene oxide product. It would be desirable, therefore, to develop a process for the epoxidation of alkene in which the efficiency is greater than that obtained in conventional commercial processes, e.g., with ethylene, efficiencies of 84 percent or greater, while maintaining other performance characteristics, particularly the activity, as described below, in a satisfactory range.

The product of the efficiency and the conversion is equal to the yield, or the percentage of the alkene fed that is converted into the corresponding oxide. The definitions of conversion, efficiency and yield may be represented as follows:

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$$\% \text{ Conversion} = \frac{\text{moles alkene reacted}}{\text{moles alkene fed}} \times 100$$

$$\% \text{ Efficiency} = \frac{\text{moles alkene oxide produced}}{\text{moles alkene reacted}} \times 100$$

$$\% \text{ Yield} = \frac{\text{moles alkene oxide produced}}{\text{moles alkene fed}} \times 100$$

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Generally, in a process for the epoxidation of alkene, a reaction inlet stream containing reactants and perhaps other additional materials enters the reactor or reaction zone in which catalytic material is provided and in which favorable reaction conditions (e.g., temperature and pressure) are maintained. The reactor effluent is withdrawn or collected from the reactor. The reactor effluent contains reaction products, together with unreacted components from the reaction inlet stream.

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Since at least some alkene is generally not converted during its initial pass through the reactor, alkene is generally present in the reactor effluent. To increase the overall yield of the process, at least a portion of the alkene in the reactor effluent is returned to the reactor via a recycle stream. Means are provided for removing and recovering at least a portion of the alkene oxide from the reactor effluent, prior to recycling, to form the product stream. At least a portion of the remaining reactor effluent (after the product stream has been withdrawn) becomes the recycle stream. The recycle stream preferably contains substantially all of the alkene that was contained in the reactor effluent.

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Reactants, i.e., oxygen-containing gas and alkene, need to be continuously replaced and are pro-

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vided to the reactor by means of a makeup feedstream. In general, the makeup feedstream and the recycle stream are combined to form the reaction inlet stream which is sent into the reactor or reaction zone. Alternatively, the makeup feedstream and the recycle stream can be introduced into the reactor separately.

The epoxidation of alkene is generally carried out in the presence of a supported silver catalyst located within the reactor or reaction zone. The silver may be supported by a conventional support material, for example, alpha-alumina. The performance of the catalyst may be affected by the presence of solid, liquid or gaseous compounds which may, for example, be incorporated in the catalyst or provided via the makeup feedstream.

The activity of a reaction system is a measure of the rate of production of the desired product, e.g., ethylene oxide, for a particular reaction system at a particular temperature. In order to provide a meaningful comparison of the effectiveness of two or more reaction systems or of a single reaction system at different times, factors, such as feed rate, feed composition, temperature, and pressure, that affect the rate of production of the desired alkene oxide must be normalized or accounted for, preferably by using a standard or fixed set of operating conditions. Since the rate of production of alkene oxide is proportional to the volume of catalyst in the reaction system, the activity is usually expressed in terms of pounds of alkene oxide produced per hour per cubic foot of catalyst. It should be noted that this method of measuring activity does not take into account variations in the densities of the catalysts since the controlling factor is the volume

of the reaction system available, not the weight of catalyst which will fit into a given volume. Other factors that have an effect on the rate of production of the desired compound include the following:

- 5 (1) the composition of the reaction stream;
- (2) the gas hourly space velocity of the reaction stream;
- (3) the temperature and pressure within the reactor or reaction zone.

10 In order to compare the effectiveness of two or more reaction systems or of a single reaction system at different times, differences in factors 1 through 3 above should be minimized and/or factored into the evaluation of relative effectiveness.

15 If the activity of a reaction system is low, then, all other things being equal, the commercial value of that system will be low. The lower the activity of a reaction system, the less product produced in a unit time for a given feed rate, reactor
20 temperature, catalyst, surface area, etcetera. A low activity can render even a high efficiency process commercially impractical. In general, an activity below 4 pounds of ethylene oxide per hour per cubic foot of catalyst is unacceptable for commercial prac-
25 tice. The activity is preferably greater than 8 pounds, and in some instances an activity greater than 11 pounds of ethylene oxide per hour per cubic foot of catalyst is desired.

 Reaction systems generally deactivate over time,
30 i.e., the activity of the catalyst begins to decrease as the process is carried out. Activity may be plotted as a function of time to generate a graph showing the aging behavior of the catalyst. Experimentation for the purpose of developing an activity plot is
35 usually conducted at a set temperature since, in

general, activity can be increased by raising the reaction temperature. Alternatively, an activity plot can be a graph of the temperature required to maintain a given activity versus time. The rate at which activity decreases, i.e., the rate of deactivation at a given point in time, can be represented by the slope of the activity plot, i.e., the derivative of activity with respect to time:

$$\text{deactivation} = d[\text{activity}]/dt.$$

The average rate of deactivation over a period of time can be represented then by the change in activity divided by the time period:

$$\text{average deactivation} = \Delta \text{activity} / \Delta t.$$

At some point, the activity decreases to an unacceptable level, for example, the temperature required to maintain the activity of the system becomes unacceptably high or the rate of production becomes unacceptably low. At this point, the catalyst must either be regenerated or replaced. The useful life of a reaction system is the length of time that reactants can be passed through the reaction system during which acceptable activity is observed. The area under a plot of activity versus time is equal to the number of pounds of alkene oxide produced during the useful life of the catalyst per cubic foot of catalyst. The greater the area under such a plot, the more valuable the process is since regeneration or replacement of the catalyst involves a number of expenses, sometimes referred to as turn-around costs. More specifically, the replacement of the catalyst generally requires that the reactor be

shut down for an extended period of time, e.g., two weeks or more, to discharge the catalyst, clean the reactor tubes, etcetera. This operation requires extra manpower and the use of special equipment. The costs involved, which may include replacement catalyst, can mount into the millions of dollars.

As used herein, an activity-reducing compound refers to a compound which, when present in an activity-reducing amount, causes a reduction in activity, some or all of which activity may subsequently be regained by returning to a situation in which the concentration of the compound is below the minimum activity-reducing amount. The minimum activity-reducing amount varies depending on the particular system, the feedstream and the activity-reducing compound.

Conversely, deactivation, as used herein, refers to a permanent loss of activity, i.e., a decrease in activity which cannot be recovered. As noted above, activity can be increased by raising the temperature, but the need to operate at a higher temperature to maintain a particular activity is representative of deactivation. Catalysts tend to deactivate more rapidly when reaction is carried out at higher temperatures.

As previously noted, since the work of Lefort (U. S. Patent 1,998,878), research efforts have been directed toward improving the performance characteristics of reaction systems, i.e., improving the activity, efficiency and useful life. Research has been conducted in areas such as feedstream additives, removal of materials in the recycle stream and methods of catalyst preparation, including the deposition or impregnation of a particular type or form of silver. Additionally, research efforts have

been directed toward the composition and formation of the support, as well as toward additives deposited on or impregnated in the support.

5 One of the difficulties in carrying out research is the necessity of considering the interrelationship of the various variables. The improvement or enhancement of one performance characteristic must not be at the expense of, or have too great an adverse effect on, one of the other performance characteristics. For example, if a reaction system is designed 10 which has a very short useful life, the system may be commercially impractical even though the efficiency and initial activity of the catalyst are outstanding. Accordingly, a system that provides an increase 15 in the efficiency of the overall catalytic reaction system, while only minimally affecting the activity and useful life of the catalyst, would be particularly beneficial.

Diluents have generally been included in the 20 gaseous mixture to reduce the likelihood of explosion. Diluents are generally supplied via the makeup feedstream. Such diluent materials have generally been believed to be inert, i.e., their function is primarily to act as a heat sink and to dilute the 25 gaseous mixture. Nitrogen has been found to be a suitable diluent material. It is well known to use air to supply both oxygen and nitrogen to the reaction zone. Another material that has been used as a diluent is carbon dioxide. EPO Patent 3642 discloses 30 that a diluent, for example, helium, nitrogen, argon, carbon dioxide, and/or a lower paraffin, for example, ethane and/or methane, may be present in proportions of 10-80 percent and preferably 40-70 percent by volume in total. Similarly, U. K. Patent Application 35 GB 2 014 133A mentions carbon dioxide as a possible

diluent. Other patents, e.g., U. S. Patents 3,043,854, 4,007,135, and 4,206,128, Japanese Patent 53-39404, and U. K. Patents 676,358 and 1,571,123, also mention that carbon dioxide is suitable for use as an additive.

5 Lefort, in U. S. Patent 1,998,878 (Re. 20,370), states that carbon dioxide may be introduced into the reactor to limit the rate of complete oxidation of ethylene to carbon dioxide. Similar disclosure is
10 found in U. S. Patent 2,270,780. U. S. Patent 2,615,900 discloses a process for producing ethylene oxide in which carbon dioxide gas may be added to the feed gases to act as a "depressant" or "anti-catalytic material". U. S. Patent 4,007,135 discloses a
15 process in which, according to the patent, carbon dioxide may be used to raise the selectivity of the reaction. According to Chem. Abstracts, Vol. 80, Issue 11, Section 22, Abstract 059195, the presence of carbon dioxide tends to retard the deactivation of
20 the silver catalyst.

As mentioned above, any alkene contained in the reactor effluent stream is preferably returned to the reaction zone via a recycle stream. It is sometimes preferred to remove some of the gas contained in the
25 reactor effluent stream via a purge stream prior to introducing the recycle stream into the reaction zone. The purge stream may comprise a straight purge, i.e., the purge stream can merely draw off a percentage of the recycle stream. Since a straight
30 purge stream generally has a composition substantially similar to that of the stream from which it is removed, some alkene will generally be purged when a straight purge is employed. For this reason, means are sometimes provided to ensure that purge streams
35 have relatively high concentrations of materials

other than alkene, such as nitrogen and carbon dioxide.

U. S. Patent 2,241,019 discloses a process in which the purge gas is carried through and in contact with an adsorptive agent which is adapted to adsorb selectively the ethylene content of the purge gas, while the nitrogen and much of the carbon dioxide present in the purge gas pass through the adsorption agent and are discharged to the atmosphere.

U. S. Patent 2,376,987 discloses a process for the two-stage preparation of butadiene in which, in the first stage, ethylene is oxidized in a converter to form ethylene oxide. The converter contains an oxidizing catalyst which is preferably finely divided silver on a carrier such as alumina. According to the patent, if concentrated oxygen is used as the oxygen source, the ethylene in the stream containing the oxidation products from the converter may be concentrated and recycled to the process by scrubbing to remove carbon dioxide, etcetera.

U. S. Patent 2,653,952 discloses a process for the manufacture of ethylene oxide in which the products from the reactor, consisting essentially of ethylene oxide, ethylene, oxygen, nitrogen, helium and carbon dioxide, are delivered to an ethylene oxide absorber. The gases are then passed in contact with a solvent for carbon dioxide. Ordinarily, ethanolamine is used as a solvent in this process. The gas discharged from the carbon dioxide absorber contains ethylene and is recycled to be again passed in contact with the catalyst in the reactor. This patent recognizes that nitrogen tends to build up to high concentrations when the oxygen is supplied by air. The process of this patent therefore employs relatively nitrogen-free oxygen in the feedstream and

dilutes the gaseous mixture with helium.

U. S. Patent 2,799,687 discloses a preferred embodiment for the oxidation of olefins in which the reactor effluent may be passed into an ethylene oxide
5 absorber after which about 70-90 percent of the effluent from the ethylene oxide absorber is recycled and the remainder plus additional oxygen is diverted to a second reactor. According to the patent, by the
10 diversion of a portion of the effluent from the first reactor to the second reactor, the buildup of carbon dioxide above certain limits, such as above about 5-7 percent, can be prevented. Similarly, U. S. Patent 4,206,128, Netherlands Patent Application 6,414,284, and U. K. Patent 1 191 983 all disclose processes in
15 which some carbon dioxide is removed from the recycle stream.

According to U. K. Patent 1,055,147, one must remove carbon dioxide from the ethylene oxide production system to keep the carbon dioxide concentration
20 in an acceptable range since, according to the patent, carbon dioxide acts as an inhibitor and suppresses the reaction of ethylene to form both ethylene oxide and carbon dioxide.

U. S. Patent 1,998,878, U. S. Patent 3,904,656,
25 "The Manufacture Of Ethylene Oxide And Its Derivatives", The Industrial Chemist, February, 1963, Kirk Othmer, "Ethylene Oxide", Volume 8, pages 534,545, "Ethylene Oxide By Direct Oxidation Of Ethylene", Petroleum Processing, November, 1955, all include, as
30 a process step, the removal of carbon dioxide from the alkene oxide for the purification of the alkene oxide product.

Since the early work on the direct catalytic oxidation of ethylene to ethylene oxide, it has been
35 suggested that the addition of certain compounds to

the gaseous feedstream or direct incorporation of metals or compounds in the catalyst could enhance or promote the production of ethylene oxide. Such metals or compounds have been known variously as "anti-catalysts", "promoters" and "inhibitors". These substances, which are not considered catalysts, are believed to contribute to the overall utility of the process by inhibiting the formation of carbon dioxide or by promoting the production of ethylene oxide.

Various compounds have been found to provide some beneficial effects when contained within the gaseous mixture supplied to the reactor. It is well known that chlorine-containing compounds, when supplied to an ethylene oxide production process, help to improve the overall effectiveness of the process. For example, Law and Chitwood, in U. S. Patent 2,194,602, disclose that higher yields of olefin oxide are obtained by retarding the complete oxidation of the olefin through the addition of very small amounts of deactivating materials (also referred to by Law and Chitwood as repressants or anti-catalytic materials) such as ethylene dichloride, chlorine, sulfur chloride, sulfur trioxide, nitrogen dioxide, or other halogen-containing or acid-forming materials. U. S. Patents 2,270,780, 2,279,469, 2,279,470, 2,799,687, 3,144,416, 4,007,135, 4,206,128, 4,368,144, EPO Patent 11 356, U. K. Patents 676,358, 1,055,147 and 1,571,123 also discuss the addition of halide compounds, such as ethyl chloride, ethylene dichloride, potassium chloride, vinyl chloride and alkyl chloride.

U. S. Patent 2,194,602 discloses a method for the activation of silver catalysts in which the activation is accomplished by bringing the catalyst in

contact with an aqueous solution of barium, strontium or lithium hydroxide after the catalyst has first been treated with a "repressant" such as ethylene dichloride, nitrogen dioxide, or other halogen-containing or acid-forming material.

U. S. Patents 2,279,469 and 2,279,470 disclose processes of making olefin oxides in which very small amounts, i.e., less than 0.1 percent of the total volume, of "anti-catalysts" are incorporated with the reactants. Halogens and compounds containing halogens, e.g., ethylene dichloride, and compounds containing nitrogen, e.g., nitric oxide, can be used as the anti-catalysts. According to the patents, it is possible to employ mixtures of the individual anti-catalyst substances.

U. S. Patent 3,144,416 discloses a method of manufacturing silver catalysts to be used for the oxidation of olefins. According to the patent, in order to increase the selectivity of the catalyst, a small quantity of halogen compound or nitrogen compound may be added to the reaction gas or catalyst.

EPO Patent 3642 and U. K. Patent Application GB 2 014 133A disclose processes of producing an olefin oxide by contacting an olefin with oxygen in the presence of a silver-containing catalyst and a chlorine-containing reaction modifier, for example, dichloroethane, methyl chloride, or vinyl chloride. According to these references, the catalyst performance is improved, for example, the selectivity is increased, by contacting the catalyst with a nitrate- or nitrite-forming substance, for example, a gas containing dinitrogen tetroxide, nitrogen dioxide and/or a nitrogen-containing compound, together with an oxidizing agent, such as nitric oxide and oxygen. The catalyst preferably comprises 3 to 50 per-

cent, more preferably 3 to 30 percent, by weight silver. According to the references, it is preferred that the catalyst should contain cations, for example, alkali and/or alkaline earth metal cations, as the corresponding nitrate or nitrite, particularly if the catalyst is treated with the nitrate- or nitrite-forming substance intermittently. According to the patents, suitable concentrations of the cations may be, for example, 5×10^{-5} to 2, preferably 5×10^{-4} to 2, more preferably 5×10^{-4} to 0.5, gram equivalents per kilogram of catalyst. Suitably, Mo, K, Sr, Ca and/or Ba are present in amounts of 2 to 20,000, preferably 2 to 10,000, more preferably 10 to 3,000, microgram equivalents per gram of silver. In the processes of these two references, a diluent, for example, carbon dioxide, may be present and unconverted olefin may be recycled, suitably after removal of carbon dioxide.

Rumanian Patent No. 53012, published December 2, 1971, discloses a process in which the catalyst is brought in direct contact with a gas mixture composed of 5-15 percent oxygen, 8-20 percent carbon dioxide, 60-80 percent nitrogen, completed by 1-5 percent nitrogen oxides.

U. K. Patent 524,007 discloses a method for activating catalysts which may be accomplished by contacting the catalyst with an aqueous solution of a hydroxide of lithium, after the catalyst has first been treated with an "anti-catalyst", such as ethylene dichloride or nitrogen dioxide. According to the patent, the treatment may most advantageously be conducted simultaneously with the oxidation reaction of the olefins, inasmuch as the presence of very small amounts of anti-catalyst (less than 0.1 percent) increases the efficiency by limiting the

formation of carbon dioxide.

Scientific literature is replete with examples of the use of alkali metals and alkaline earth metals and their cations to promote the efficiency of silver catalysts used in epoxidation reactions. Numerous examples may be found in literature regarding preference for the inclusion or exclusion of one or several metals or cations in silver catalysts. Although many reports have indicated that no particular effectiveness is observed with one alkali metal or alkaline earth metal cation vis-a-vis another, several have suggested clear preferences for particular metal cations.

Potassium is well known as a catalyst promoter for the epoxidation of alkenes. One of the first patents to recognize potassium as a suitable promoter was U. S. Patent 2,177,361. According to this patent, the catalyst may be promoted by the presence of very small proportions of alkali or alkaline earth metals.

U. K. Patent Application 2,122,913A discloses a catalyst and a process for oxidation of ethylene in which an amount of alkali metal is deposited on the catalyst which removes substantially all activity from the silver catalyst and then activity and selectivity are recovered by heating the catalyst in a nitrogen atmosphere.

When potassium is employed in the catalyst, it is generally introduced in conjunction with an anion. The choice of the anion has not always been regarded as significant. For example, U. S. Patents 3,962,136, 4,010,115, 4,012,425, and 4,356,312 state that no unusual effectiveness is observed with the use of any particular anion in the alkali metal salts used to prepare the catalysts and suggests that ni-

trates, nitrites, chlorides, iodides, bromates, etcetera, may be used. Potassium nitrate was employed in the silver salt solution of Example 1 in each patent. According to the patents, from about 4.0×10^{-5} to about 8.0×10^{-3} gram equivalent weights of ionic higher alkali metal, e.g., rubidium, cesium or potassium or mixtures thereof, per kilogram of catalyst is deposited on the catalyst support simultaneously with the deposit of silver. The amount of higher alkali metal preferably ranges from about 2.0×10^{-4} to about 6.5×10^{-3} gram equivalent weights per kilogram of finished catalyst. According to the patents, the amount of the higher alkali metal (or metals) present on the catalyst surface is critical and is a function of the surface area of catalyst. According to the patents, the alkali metal is present in final form on the support in the form of its oxide. U. S. Patents 3,962,136, 4,010,115 and 4,012,425 note that the highest level of selectivity obtainable when potassium is employed typically is lower than that obtainable when rubidium or cesium is employed while U. S. Patent 4,356,312 notes that particularly good results are obtained with potassium.

U. S. Patent 4,066,575 notes that alkali metal nitrate is suitable for supplying an alkali metal promoter, but it notes that the anion associated with the promoter metal is not critical. U. S. Patent 4,207,210 discloses a process for preparing an ethylene oxide catalyst in which higher alkali metals, such as potassium, rubidium and cesium, are deposited on a catalyst support prior to the deposition of silver. According to the patent, the amount of higher alkali is a critical function of the surface area of the support. This patent also notes that no un-

usual effectiveness is observed with the use of any particular anion in preparing the catalysts and lists nitrates as one type of salt that may be used. Carbon dioxide and steam are listed as diluent materials.

The use of potassium nitrate, however, to impart a promoting effect on the catalyst has been widely described. For example, U. S. Patent 4,007,135 lists a number of materials, including potassium, which can be used as promoters. According to the patent, in general, 1 to 5,000, preferably 1 to 1,000, more preferably 40 to 500, and particularly 20 to 200, atoms of potassium are present per 1,000 atoms of silver. Suitably an aqueous solution of a compound, such as a chloride, sulfate, nitrate, nitrite, etcetera, of the promoter is used for impregnation. U. S. Patent 4,094,889 discloses a process for restoring the selectivity of silver catalysts in which alkali metal may be introduced as a nitrate and in which the preferred content of potassium is in the range of 2×10^{-2} to 3×10^{-5} grams/square meter of surface area of support. U. S. Patent 4,125,480 discloses a process for reactivating used silver catalyst comprising (a) washing the used catalyst, and (b) depositing from 0.00004 to 0.008, preferably from 0.0001 to 0.002 gram equivalent weights per kilogram of catalyst of ions of one or more of the alkali metals, such as sodium, potassium, rubidium, or cesium. The ions of, e.g., potassium are deposited on the catalyst by impregnating it with a solution of one or more compounds, such as potassium nitrate. U. S. Patents 4,226,782, 4,235,757, 4,324,699, 4,342,667, 4,368,144, 4,455,392, Japanese Patent 56/89843, and U. K. Patent 1,571,123 suggest the use of potassium nitrate in various amounts.

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Potassium nitrate may also be formed in situ when a carrier material is treated with certain amines in the presence of potassium ions, for example, when silver is introduced to a carrier material in a silver-impregnating solution containing an amine and potassium ions, followed by roasting.

There has been some disclosure directed to catalysts for use in an ethylene oxide production system in which silver is present in relatively large proportions, e.g., 35 percent or more. For example, U. S. Patents 3,565,828 and 3,654,318 disclose catalysts for the synthesis of ethylene oxide from oxygen and ethylene. According to the patents, the catalysts contain from 60 percent to 70 percent by weight of silver.

U. S. Patent 2,593,099 discloses a magnesium oxide-barium oxide silver catalyst support. According to the patent, the conventional amount of silver is deposited on the support, namely, 2 to 50 percent, with the best results being obtained between 4 and 20 percent.

U. S. Patent 2,713,586 discloses a process for the oxidation of ethylene to ethylene oxide in which, according to the patent, the conventional amount of silver is deposited on the support, namely, 5 to 50 percent, with the best results being obtained between 4 and 20 percent.

U. S. Patent 3,793,231 discloses a process for the preparation of silver catalysts for the production of ethylene oxide in which the silver content of the catalysts generally range between 15 to 30 percent by weight, preferably 19 to 27 percent by weight.

A large body of art directed to various aspects of alkene oxide production has been developed over

the years since Lefort (U. S. Patent 1,998,878). Much of it is contradictory and incapable of reconciliation. None of the art is believed to recognize or suggest that carbon dioxide can have a deleterious
5 effect on the activity of a high efficiency epoxidation system as defined herein.

Disclosure of the Invention:

10 When excessive carbon dioxide is present in the reaction zone of a high efficiency epoxidation system, the activity of such a system is lower than when less carbon dioxide is present. By reducing the concentration of carbon dioxide, the activity-reduc-
15 ing effect of excessive carbon dioxide can be reduced. By excessive carbon dioxide is meant a concentration of carbon dioxide at which activity-reducing effects are observed. The concentration of carbon dioxide at which activity-reducing effects begin
20 to be seen may vary from system to system.

The present invention provides a high-efficiency process for the epoxidation of alkene, for example, ethylene, to form the corresponding alkene oxide by contacting alkene and oxygen-containing gas in a
25 reaction zone under epoxidation conditions in the presence of at least one gaseous efficiency-enhancing member of a redox-half reaction pair (sometimes referred to herein as a gaseous efficiency-enhancing compound), preferably nitric oxide and/or nitrogen
30 dioxide and a supported silver catalyst. The catalyst comprises a catalytically-effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt of a member of a redox-half reaction pair, preferably potassium nitrate, on
35 a support. The contacting may be carried out further

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in the presence of performance-enhancing gaseous halide, such as 1,2-dichloroethane and/or ethyl chloride. The reactor effluent or outlet stream comprises alkene oxide, carbon dioxide, and unreacted
5 alkene. At least a portion of the alkene oxide in the reactor effluent is removed as the product. In accordance with the discovery that excessive carbon dioxide is deleterious to the activity of a high efficiency reaction system, sufficient carbon dioxide
10 is removed from the recycle stream that the activity-reducing effect of carbon dioxide is diminished.

Brief Description Of The Drawing:

15 Figure 1 is a flow chart of a process in accordance with the invention.

Detailed Description Of The Invention:

20 The present invention is directed to high-efficiency processes for the epoxidation of alkene to form alkene oxide by contacting alkene and oxygen-containing gas under epoxidation conditions in the presence of a gaseous efficiency-enhancing member of
25 a redox-half reaction pair and a supported silver catalyst. The silver catalyst generally comprises a catalytically-effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt of a member of a redox-half reaction
30 pair on a porous support. A gaseous halide may also be present in the reaction zone. As used herein, a high-efficiency process refers to an epoxidation process in which the efficiency for conversion of alkene to alkene oxide is higher than that typically
35 obtained in a commercial process. For instance, when

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ethylene is used, efficiencies of at least 84 percent are achieved by the process of this invention.

It has been found that with high efficiency reaction systems, such as those contemplated by the present invention, the presence of excessive carbon dioxide in the reaction zone has an activity-reducing effect. The concentration at which carbon dioxide becomes excessive, i.e., has an activity-reducing effect, may vary depending on the particular reaction system. For example, concentrations of carbon dioxide in the reaction inlet stream greater than about 1 volume percent have been found to reduce activity of ethylene epoxidation systems.

Carbon dioxide is generally continuously produced as a by-product of the alkene epoxidation reaction. As a result, carbon dioxide is generally contained in the reactor effluent and, unless removed, some portion of it is normally returned to the reaction zone via the recycle stream. According to the invention, sufficient carbon dioxide is removed from the recycle stream that the activity-reducing effects of carbon dioxide are diminished.

The following description of the preferred system for epoxidation of alkene in accordance with the present invention may be better understood by reference to the flow chart in Figure 1.

In steady-state operation of the preferred system, a reaction inlet stream containing reactants, together with other gaseous materials as discussed below, is fed to a reactor at a controlled gas hourly space velocity (GHSV). The reactor may take a variety of forms, but is preferably a collection of vertical tubes containing a supported silver catalyst. The reaction inlet stream enters the reactor, passes through the catalyst, and exits the reactor as the

reactor effluent. The desired product, e.g., ethylene oxide, is separated from the other components in the reactor effluent, preferably by a scrubbing operation. The remainder of the reactor effluent becomes
5 the recycle stream. It is sometimes preferred to remove a portion of the material in the recycle stream in order to, for example, prevent buildup of certain materials in the system. The removal of material from the recycle stream may be selective,
10 i.e., certain compounds may be removed from the recycle stream in greater proportions than other compounds. The remainder of the recycle stream is usually combined with a makeup feedstream to form the reaction inlet stream. The reaction system will be
15 discussed in greater detail below.

Although the present invention can be used with any size and type of alkene oxide reactor, including both fixed bed and fluidized bed reactors, it is contemplated that the present invention will find
20 most widespread application in standard fixed bed, multi-tubular reactors. These generally include wall-cooled as well as adiabatic reactors. Tube lengths typically range from about 5 to about 60 feet (1.52 to 18.3 meters), frequently from about 15 to
25 about 40 feet (1.52 to 12.2 meters). The tubes generally have internal diameters from about 0.5 to about 2 inches (1.27 to 5.08 centimeters), typically from about 0.8 to about 1.5 inches (2.03 to 3.81 centimeters).

30 The catalyst generally comprises a support having catalyst material or a mixture of catalyst material and an efficiency-enhancing material impregnated or coated on the support. The support can be generally described as a porous, inorganic substrate which
35 is not unduly deleterious to the performance of the

system and is preferably substantially inert toward the other materials in the system, i.e., the catalyst material, any other components present in the catalyst, e.g., efficiency-enhancing salt, and components in the reaction inlet stream. In addition, the support should be able to withstand the temperatures employed within the reactor, as well as, of course, the temperatures employed in manufacturing the catalyst, e.g., if the catalyst material is reduced to its free metallic state by roasting. Suitable supports for use in accordance with the present invention include silica, magnesia, silicon carbide, zirconia, and alumina, preferably alpha-alumina. The support preferably has a surface area of at least about 0.7 m²/g, preferably in the range of from about 0.7 to about 16 m²/g, more preferably about 0.7 to about 7 m²/g. The surface area is measured by the B. E. T. nitrogen method described by Brunauer, Emmet and Teller in J. Am. Chem. Soc. 60, 309-316 (1938).

The support may be composed of a particulate matrix. In a preferred support, at least about 50 percent of the total number of support particles having a particle size greater than about 0.1 micrometer have at least one substantially flat major surface. The support particles are preferably formed into aggregates or "pills" of such a size and shape that they are readily usable in commercially operated tubular reactors. These aggregates or pills generally range in size from about 2 millimeters to about 15 millimeters, preferably about 3 millimeters to about 12 millimeters. The size is chosen to be consistent with the type of reactor employed. In general, in fixed bed reactor applications, particle sizes ranging from about 3 millimeters to about 10 millimeters have been found to be most suitable in the typical

tubular reactors used in commerce.

The shapes of the carrier aggregates useful for purposes of the present invention can vary widely. Common shapes include spheres and cylinders, especially hollow cylinders.

The preferred support particles in accordance with the present invention have at least one substantially flat major surface and may be characterized as having a lamellate or platelet-type morphology. Some of the particles have two, or sometimes more, flat surfaces. The major dimension of a substantial portion of the particles having platelet-type morphology is less than about 50 microns, preferably less than about 20 microns. When alpha-alumina is employed as the support material, the platelet-type particles frequently have a morphology which approximates the shape of hexagonal plates.

The carrier materials of the present invention may generally be described as porous or microporous and they generally have median pore diameters of from about 0.01 to about 100 microns, preferably about 0.5 to about 50 microns, and most preferably about 1 to about 5 microns. Generally, they have pore volumes of about 0.6 to about 1.4 cc/g, preferably about 0.8 to about 1.2 cc/g. Pore volumes may be measured by any conventional technique, such as conventional mercury porosity or water absorption techniques.

Generally improved results have been demonstrated when the support material is composition-pure and also phase-pure. By "composition-pure" is meant a material which is substantially a single substance, such as alumina, with only trace impurities being present. The term "phase-pure" refers to the homogeneity of the support with respect to its phase. In the present invention, alumina, having a high or

exclusive alpha-phase purity (i.e., alpha-alumina) is preferred. Most preferred is a material composed of at least 98 percent, by weight, alpha-alumina.

Under some conditions even small amounts of
5 leachable sodium can adversely affect the service life of the catalyst. Notably improved results have been observed when the support contains less than about 50 parts per million (ppm) by weight, preferably less than 40 ppm, based on the weight of the
10 total catalyst. The term leachable sodium, as used herein, refers to sodium which can be removed from the support by immersing the support in a 10 percent by volume nitric acid solution at 90 degrees C for one hour. Suitable alpha-aluminas having concentra-
15 tions of sodium below 50 ppm may be obtained commercially from suppliers such as the Norton Company. Alternatively, suitable alpha-alumina support materials may be prepared so as to obtain leachable sodium concentrations below 50 ppm by the method de-
20 scribed by Weber et al in U. S. Patent 4,379,134.

A particularly preferred support is a high-purity alpha-alumina support, having platelet morphology, of the type disclosed in Canadian Patent Application Serial Number
25 515,864-8, filed August 13, 1986.

The present invention includes in the catalyst
30 at least one efficiency-enhancing salt of a member of a redox-half reaction pair. The term "redox-half reaction" is defined herein to mean half-reactions such as those found in equations presented in tables of standard reduction or oxidation potentials, also
35 known as standard or single electrode potentials.

These equations are found in, for instance, "Handbook of Chemistry", N. A. Lange, Editor, McGraw-Hill Book Company, Inc., pages 1213-1218 (1961) or "CRC Handbook of Chemistry and Physics", 65th Edition, CRC Press, Inc., Boca Raton, Florida, pages D 155-162 (1984). The term "redox-half reaction pair" refers to the pairs of atoms, molecules or ions, or mixtures thereof, which undergo oxidation or reduction in such half-reaction equations. A member of a redox-half reaction pair is, therefore, one of the atoms, molecules or ions that appear in a particular redox-half reaction equation. The term redox-half reaction pair is used herein to include those members of the class of substances which provide the desired performance enhancement rather than a mechanism of the chemistry occurring. Preferably, such compounds, when associated with the catalyst as salts of members of a redox-half reaction pair, are salts in which the anions are oxyanions, preferably an oxyanion of a polyvalent atom, i.e., the atom of the anion to which oxygen is bonded is capable of existing, when bonded to a dissimilar atom, in different valence states. The preferred efficiency-enhancing salts are potassium nitrate and potassium nitrite.

The catalysts of the present invention are preferably prepared by depositing catalyst material and at least one efficiency-enhancing salt, sequentially or simultaneously, on and/or within a solid porous support. The preferred catalyst material in accordance with the present invention comprises silver, preferably of a particle size less than about 0.5 micron. Any known method of introducing the catalyst material and efficiency-enhancing salt into the catalyst support may be employed, but it is preferred that the support is either impregnated or coated.

The more preferred of these is impregnation wherein, in general, a solution of a soluble salt or complex of silver and/or one or more efficiency-enhancing salt is dissolved in a suitable solvent or "complex-
5 ing/solubilizing" agent. This solution may be used to impregnate a porous catalyst support or carrier by immersing the carrier in the silver- and/or efficiency-enhancing salt-containing impregnation solution.

Sequential impregnation means that silver is
10 first deposited within the carrier in one or more impregnation steps, and then salt is deposited in a separate impregnation step.

One aspect of the present invention involves the beneficial effects observed when the catalyst con-
15 tains high concentrations of silver. In order to provide such a catalyst by impregnation, it has been found that it is preferable to deposit the silver via several impregnation steps. Thus, if a high silver-content catalyst, e.g., a catalyst containing 30 or
20 more percent silver, is desired and a sequential impregnation procedure is to be used, a four-step process may be employed. Such a process would involve three silver-only impregnation steps followed by one salt-only impregnation step.

25 In general, a silver-only impregnation step is carried out by first immersing the support in a silver-containing impregnation solution, preferably by placing the support particles in a vessel, evacuating the vessel and then adding the impregnation solu-
30 tion. The excess solution may then be allowed to drain off or the solvent may be removed by evaporation under reduced pressure at a suitable temperature. Typically, a silver-containing solution is prepared by dissolving silver oxide in a suitable
35 solvent or complexing/solubilizing agent as, for

example, a mixture of water, ethylenediamine, oxalic acid, silver oxide, and monoethanolamine.

After impregnation, the silver-impregnated carrier particles are treated to convert silver salt to silver metal to effect deposition of silver on the surface of the support. This may be done by treating the impregnated particles with a reducing agent, such as oxalic acid, alkanolamine or by roasting at an elevated temperature on the order of about 100 to about 900 degrees C, preferably about 200 to about 650 degrees C, to decompose the silver compound and reduce the silver to its free metallic state. The duration of roasting is generally for a period of from about 1 to about 10 minutes, with longer times for lower temperatures, depending on the temperature used. As used herein, the term "surface", as applied to the support, not only includes the external surfaces of the carrier but also the internal surfaces, that is, the surfaces defining the pores or internal portion of the support particles.

The efficiency-enhancing salt may be introduced into the catalyst in any suitable manner. In general, the preferred amount of efficiency-enhancing salt can be deposited in one impregnation step. After immersion of the silver loaded support in the efficiency-enhancing salt impregnation solution, the excess solution is generally drained and the silver- and efficiency-enhancing salt-containing support is dried, for example by heating to from 80 to 200 degrees C. When more than one salt of a member of a redox-half reaction pair is employed, the salts may be deposited together or sequentially.

Concurrent or coincidental impregnation means that generally the final (perhaps the only) impregnation step involves immersion of the support in an

impregnation solution which contains silver as well as one or more efficiency-enhancing salts. Such an impregnation step may or may not be preceded by one or more silver-only impregnation steps. Thus, to
5 make a high silver-content catalyst by coincidental impregnation, several silver-only impregnation steps might be carried out, followed by a silver- and efficiency-enhancing salt-impregnation step. A low silver-content catalyst, e.g., from about 2 to about 20
10 weight percent silver, may be made by a single silver- and efficiency-enhancing salt-impregnation step. For the purposes of this invention, these two sequences are both referred to as concurrent or coincidental impregnation.

15 The three types of impregnation solutions, namely, silver-containing, efficiency-enhancing salt-containing, and silver- and efficiency-enhancing salt-containing, are discussed in more detail below.

There are a large number of suitable solvents or
20 complexing/solubilizing agents which may be used to form the silver-containing impregnating solution. A suitable solvent or complexing/solubilizing agent, besides adequately dissolving the silver or converting it to a soluble form, should be capable of being
25 readily removed in subsequent steps, either by a washing, volatilizing or oxidizing procedure, or the like. It is also generally preferred that the solvents or complexing/solubilizing agents be readily
30 miscible with water since aqueous solutions may frequently be employed.

Among the materials found suitable as solvents or complexing/solubilizing agents for the preparation of the silver-containing solutions are alcohols, including glycols, such as ethylene glycol, ammonia,
35 amines and aqueous mixtures of amines, such as ethy-

lenediamine and monoethanolamine, and carboxylic acids, such as oxalic acid and lactic acid.

The particular silver salt or compound used to form the silver-containing impregnating solution in a solvent or a complexing/solubilizing agent is not particularly critical and any known silver salt or compound generally known to the art which is soluble in and does not react with the solvent or complexing/solubilizing agent may be employed. Thus, the silver may be introduced into the solvent or complexing/solubilizing agent as an oxide, a salt, such as a nitrate or carboxylate, for example, an acetate, propionate, butyrate, oxalate, lactate, citrate, phthalate, generally the silver salts of higher fatty acids, and the like.

Materials which may be employed in the efficiency-enhancing salt-containing impregnation solution to act as a solvent for the efficiency-enhancing salt include generally any solvent capable of dissolving the salt, which solvent will neither react with the silver nor leach silver from the support. Aqueous solutions are generally preferred but organic liquids, such as alcohols, may also be employed.

In order to perform coincidental impregnation, the efficiency-enhancing salt and the silver catalyst material must both be soluble in the solvent or complexing/solubilizing liquid used.

Suitable results have been obtained with both the sequential and coincidental procedures. Some results have indicated that greater amounts of silver with more uniform distribution of silver throughout the pill can be obtained by three or more silver-impregnation cycles. High silver-containing catalysts prepared by a coincidental impregnation technique generally provide better initial performance than

those prepared by a sequential technique.

If the catalyst material is to be coated on the catalyst support rather than impregnated in the support, the catalyst material, e.g., silver, is pre-
5 formed or precipitated into a slurry, preferably an aqueous slurry, such that the silver particles are deposited on the support and adhere to the support surface when the carrier or support is heated to removed the liquids present.

10 The concentration of silver in the finished catalyst may vary from about 2 percent to 60 percent or higher, by weight, based on the total weight of the catalyst, more preferably from about 8 percent to about 50 percent, by weight. When a high silver
15 content catalyst is employed, a silver concentration range of from about 30 to about 60 percent, by weight, is preferred. When a lower silver content catalyst is used, a preferred range is from about 2 to about 20 weight percent. The silver is preferably
20 distributed relatively evenly over the support surfaces. The optimum silver concentration for a particular catalyst must take into consideration performance characteristics, such as catalyst activity, system efficiency and rate of catalyst aging, as well
25 as the increased cost associated with greater concentrations of silver in the catalyst material. The approximate concentration of silver in the finished catalyst can be controlled by appropriate selection of the number of silver-impregnation steps and of the
30 concentration of silver in the impregnation solution or solutions.

The amount of the efficiency-enhancing salt of a member of a redox-half reaction pair present in the catalyst directly affects the activity and efficiency
35 of the epoxidation reaction. The most preferable

amount of the salt of a member of a redox-half reaction pair varies depending upon the alkene being epoxidized, the compound used as the gaseous efficiency-enhancing member of a redox-half reaction pair, the concentration of components in the reaction inlet stream, particularly the gaseous efficiency-enhancing compound and carbon dioxide, the amount of silver contained in the catalyst, the surface area, morphology and type of support, and the process conditions, e.g., gas hourly space velocity, temperature, and pressure. The preferred efficiency-enhancing salt is potassium nitrate.

It has been noted that when conventional analyses have been conducted with catalysts prepared by co-impregnation with silver and efficiency-enhancing salt, not all the anion associated with the cation has been accounted for. For example, catalysts prepared by co-impregnation with a potassium nitrate solution have been analyzed by conventional techniques and about 3 moles of the nitrate anion have been observed for every 4 moles of the potassium cation. This is believed to be due to limitations in the conventional analytical techniques and does not necessarily mean that the unaccounted for anions are not nitrate. For this reason, the amount of the efficiency-enhancing salt in the catalyst is given, in some instances, in terms of the weight percentage of the cation of the efficiency-enhancing salt (based on the weight of the entire catalyst), with the understanding that the anion associated with the cation is also present in the catalyst in an amount roughly proportional (on a molar basis) to the cation.

It is generally preferable that the efficiency-enhancing salt be provided in such an amount that the finished catalyst contains from about 0.01 to about

5.0 percent, by weight, of the cation of the salt, based on the total weight of the catalyst, more preferably from about 0.02 to about 3.0 weight percent, most preferably from about 0.03 to about 2.0 weight percent. The approximate concentration of efficiency-enhancing salt in the finished catalyst can be controlled by appropriate selection of the concentration of efficiency-enhancing salt in the salt-impregnation solution.

When more than one salt of a member of a redox-half reaction pair is employed, the salts may be deposited together or sequentially. It is preferred, however, to introduce the salts to the support in a single solution, rather than to use sequential treatments using more than one solution and a drying step between impregnation steps, since the latter technique may result in leaching the first introduced salt by the solution containing the second salt. Concurrent or coincidental impregnation may be accomplished by forming an impregnating solution which contains the dissolved efficiency-enhancing salt of a member of a redox-half reaction pair as well as silver catalyst material. Silver-first impregnation can be accomplished by impregnating the support with the silver-containing solution, drying the silver-containing support, reducing the silver, and impregnating the support with the efficiency-enhancing salt solution.

Reaction conditions maintained in the reactor during operation of the process are those typically used in carrying out epoxidation reactions. Temperatures within the reaction zone of the reactor generally range from about 180 to about 300 degrees C and pressures generally range from about 1 to about 30 atmospheres, typically from about 10 to about 25

atmospheres. The gas hourly space velocity (GHSV) may vary, but it will generally range from about 1,000 to about 16,000 hr⁻¹.

5 The product, for example, ethylene oxide, is recovered from the reactor effluent, e.g., by an absorption process. One such method comprises supplying the reactor effluent stream to the bottom of an absorption column while adding a solvent, for example, water, to the top of the absorption column. 10 The solvent preferably absorbs the ethylene oxide and carries it out of the bottom of the absorption column, while the remainder of the reaction effluent passes out of the top of the absorption column to form the recycle stream. The desired product 15 is thereafter recovered, for example, by passing the solvent and absorbed product through a stripper.

As noted above, it may be preferable to remove a portion of the recycle stream prior to returning the recycle stream to the reaction zone. It is generally 20 preferable to selectively remove certain compounds. An absorption column or other types of separation means can be used to provide a selective purge.

The recycle stream generally contains the diluents and inhibitors fed to the system, unreacted 25 alkene and oxygen, together with by-products of the reaction, such as carbon dioxide and water, and any minor amount of alkene oxide which is not recovered as product. After removal of the purge stream, the recycle stream is returned to the reaction zone, 30 preferably being mixed with the makeup feedstream prior to or as it enters the reaction zone.

The makeup feedstream replaces reactants, i.e., alkene and oxygen-containing gas, as well as other materials not contained in the recycle stream in 35 sufficient amounts. Alkene, as used herein, refers

to cyclic and acyclic alkenes which are in a gaseous state or have significant vapor pressures under epoxidation conditions. Typically these compounds are characterized as having on the order of 12 carbon atoms or less and which are gaseous under epoxidation conditions. In addition to ethylene and propylene, examples of alkenes which may be used in the present invention include such compounds as butene, dodecene, cyclohexene, 4-vinylcyclohexene, styrene, and norbornene.

The oxygen-containing gas employed in the reaction may be defined as including pure molecular oxygen, atomic oxygen, any transient radical species derived from atomic or molecular oxygen capable of existence under epoxidation conditions, mixtures of another gaseous substance with at least one of the foregoing, and substances capable of forming one of the foregoing under epoxidation conditions. Such oxygen-containing gas is typically oxygen introduced to the reactor either as air, commercially pure oxygen or any other gaseous substance which forms oxygen under epoxidation conditions.

The makeup feedstream may also contain one or more additives, for example, a performance-enhancing gaseous halide, preferably an organic halide, including saturated and unsaturated halides, such as 1,2-dichloroethane, ethyl chloride, vinyl chloride, methyl chloride, and methylene chloride, as well as aromatic halides. The performance-enhancing gaseous halide preferably comprises 1,2-dichloroethane and/or ethyl chloride. In addition, a hydrocarbon, such as ethane, can be included in the makeup feedstream. The makeup feedstream may also contain a diluent or ballast, such as nitrogen, as is the case when air is used as the oxygen-containing gas.

The makeup feedstream generally also includes at least one gaseous efficiency-enhancing member of a redox-half reaction pair. The phrase "gaseous efficiency-enhancing compound", as used herein, is an alternative expression for the expression "at least one gaseous efficiency-enhancing member of a redox-half reaction pair." Both phrases are therefore meant to include single gaseous efficiency-enhancing members of redox-half reaction pairs as well as mixtures thereof. The term "redox-half reaction pair" has essentially the same meaning as defined in connection with efficiency-enhancing salts, above. The preferred gaseous efficiency-enhancing materials are, preferably, compounds containing oxygen and an element capable of existing in more than two valence states. Examples of preferred gaseous efficiency-enhancing members of redox-half reaction pairs include NO, NO₂, N₂O₄, N₂O₃, any substance capable of forming gaseous NO and/or NO₂ under epoxidation conditions, or mixtures thereof. In addition, mixtures of one of the compounds listed above, particularly NO, with one or more of PH₃, CO, SO₃, and SO₂ are suitable. Nitric oxide is particularly preferred.

In some cases it is preferable to employ two members of a particular half-reaction pair, one in the efficiency-enhancing salt and the other in the gaseous efficiency-enhancing compound employed in the feedstream, as, for example, with a preferred combination of KNO₃ and NO. Other combinations, such as KNO₃/N₂O₃, KNO₃/NO₂, and KNO₂/N₂O₄ may also be employed in the same system. In some instances, the salt and the gaseous members may be found in half-reactions which represent the first and last reactions in a series of half-reaction equations of an overall reaction.

The gaseous efficiency-enhancing member of a redox-half reaction pair is preferably present in an amount that favorably affects the efficiency and/or the activity. The precise amount is determined, in part, by the particular efficiency-enhancing salt employed and the concentration thereof, as well as the other factors noted above which influence the amount of efficiency-enhancing salt. Suitable ranges of concentration for the gaseous efficiency-enhancing compound are generally dependent upon the particular alkene which is being epoxidized, larger amounts of the gaseous efficiency-enhancing compound generally being preferable with higher alkenes. For example, in an ethylene epoxidation system, a suitable range of concentration for the gaseous efficiency-enhancing member of a redox-half reaction pair is typically about 0.1 to about 100 ppm by volume of the reaction inlet stream. Preferably, the gaseous efficiency-enhancing compound is present in the reaction inlet stream in an amount within the range of from 0.1 to 80 ppm, by volume, when about 3 percent, by volume, carbon dioxide is present in the reaction inlet stream. When nitric oxide is employed as the gaseous efficiency-enhancing compound in an ethylene epoxidation system, it is preferably present in an amount of from about 0.1 to about 60 ppm by volume. When about 3 percent, by volume, carbon dioxide is present in the reaction inlet stream, nitric oxide, if used as the gaseous efficiency-enhancing compound, is preferably present in an amount of from about 1 to about 40 ppm. On the other hand, in a propylene or higher alkene epoxidation system a suitable concentration of the gaseous efficiency-enhancing compound is typically higher, e.g., from about 5 to about 2,000 ppm by volume of the reaction inlet stream when using nitro-

gen ballast.

Similarly, the concentration of the performance-enhancing gaseous halide, if one is used, is dependent, inter alia, upon the particular alkene which is being oxidized. A suitable range of concentration for gaseous halide in an ethylene epoxidation system is typically from about 0.1 to about 60 ppm by volume of the reaction inlet stream. A suitable concentration for gaseous halide in the reaction inlet stream in a propylene epoxidation system is typically from about 5 to about 2,000 ppm by volume when using nitrogen ballast. The preferred concentration of gaseous halide, if one is used, varies depending on the particular compounds used as the efficiency-enhancing salt and the gaseous efficiency-enhancing compound and the concentrations thereof, as well as the other factors noted above which influence the preferred amount of efficiency-enhancing salt.

The ranges for the concentration of alkene, oxygen, hydrocarbon, carbon dioxide and nitrogen or other ballast gas such as methane, in the reaction inlet stream, are dependent upon the alkene being epoxidized. The tables below show typical ranges for the materials (other than the efficiency-enhancing compound and the gaseous halide) in the reaction inlet stream for the epoxidation of ethylene (Table A) and propylene (Table B).

Table A

<u>Component</u>	<u>Concentration</u>
5 Ethylene	at least about 2, often about 5 to about 50, volume percent
10 Oxygen	about 2 to about 8 volume percent
Hydrocarbon	about 0 to about 5 volume percent
15 Carbon Dioxide	about 0 to about 7, preferably 0 to about 5, say, about 0 to about 3, volume percent
20 Nitrogen or other ballast gas, e.g., methane	remainder
25	
30	
35	
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Table B

	<u>Component</u>	<u>Concentration</u>
5	Propylene	about 2 to about 50 volume percent
	Oxygen	about 2 to about 10 volume percent
10	Hydrocarbon	about 0 to about 5 volume percent
15	Carbon Dioxide	about 0 to about 15, preferably 0 to about 10, say, 0 to about 5, volume percent
20	Nitrogen or other ballast gas, e.g., methane	remainder

25 The ranges set out in Table B for the concentra-
tion of materials in the reaction inlet stream may be
useful for epoxidation of higher alkenes, e.g., al-
kenes having from 4 to 12 carbon atoms.

30 The invention will be better understood by ref-
erence to the following examples which are offered by
way of illustration and not by way of limitation.

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Example 1:

A supported silver catalyst made as described below under the heading Method Of Preparation Of Catalyst of Example 1 was tested in an autoclave reactor using a feedstream having the composition set out in Table I under the conditions set out in Table II. The autoclave was a backmixed, bottom-agitated "Magnedrive" TM autoclave as described in Figure 2 of the paper by J. M. Berty entitled "Reactor For Vapor Phase-Catalytic Studies" in Chemical Engineering Progress, Volume 70, Number 5, pages 78-84, 1974.

TABLE I

15

Makeup Feedstream Composition

	<u>Component</u>	<u>Amount (By Volume)</u>
20	ethylene	30 percent
	oxygen	8 percent
	chloroethane	5 ppm
	nitric oxide	11 ppm
	nitrogen	balance
25	carbon dioxide	as indicated in Table III

TABLE II

30	GHSV	8,000 hr ⁻¹
	Temperature	240 degrees C
	Pressure	275 psig
	Catalyst volume	80 cc

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Method Of Preparation Of Catalyst of Example 1:

A co-impregnation solution was prepared by placing 1,220.2 grams ethylenediamine in a vessel and
5 mixing therewith 1,200.5 grams distilled water to form a solution. To the stirred solution was slowly added 1,245.1 grams oxalic acid and, with continuous stirring, 1,962.0 grams of silver oxide were slowly added. When dissolution was complete, 460.0 grams of
10 monoethanolamine were added directly to the solution. To the silver-containing solution were added 101.4 grams of potassium nitrate. To the resulting solution was added sufficient distilled water to dilute the solution to 6,300 ml. High-purity alpha-
15 alumina support pellets (77.8 g), having a platelet morphology, of the type disclosed in Canadian Patent Application Serial No. 515,864-8, filed August 13, 1986, having a surface area of $1.12 \text{ m}^2/\text{g}$ and a porosity of 0.86 cc/g were placed in a tube which was then evacuated,
20 following which the support pellets were impregnated by immersing them in a portion of the impregnating solution formed as described above for one hour following which the excess impregnation solution was drained. The resulting pellets were then belt-
25 roasted at 500 degrees C. in a 66 SCFH air flow for 2.5 minutes. The resulting material contained 17.8 weight percent silver and 0.38 weight percent potassium.

Catalyst prepared as described above was tested
30 with no carbon dioxide in the reaction inlet stream, following which catalyst from the same production batch was tested with 2.8 volume percent carbon dioxide in the reaction inlet stream. The values for activity and efficiency for the system both in the
35 presence and in the absence of carbon dioxide, after

varying amounts of time had passed, are listed in Table III.

TABLE III

0 Volume Percent Carbon
Dioxide In Makeup Feedstream

Activity:			
lbs ethylene			
oxide/ft ³ of			
	<u>Time (Days)</u>	<u>catalyst-hr</u>	<u>Efficiency</u>
	1	17.2	89.0
15	2	16.7	89.1
	3	15.7	89.3
	4	14.9	89.1
	5	14.7	89.0
	5.6	14.4	88.9

2.8 Volume Percent Carbon
Dioxide In Makeup Feedstream

	1	6.4	86.4
25	2	5.8	86.3
	3	5.3	85.6
	4	4.9	86.0
	5	4.6	84.8
	6	4.5	85.6

As can be seen from Table III, the activity and efficiency are significantly reduced when 2.8 volume percent carbon dioxide is present in the makeup feedstream as compared to when 0 volume percent carbon dioxide is present.

Example 2 - Coincidental or
Coimpregnation Method Of Preparation
Of A Potassium Nitrate-Containing

5 Supported High Silver Concentration Catalyst:

10 A first silver-containing impregnation solution
was prepared by dissolving 1,292.8 grams ethylene-
diamine with 1,281.6 grams of distilled water and
stirring for a period of 10 minutes. To the stirred
solution were slowly added 1,294.8 grams of oxalic
acid dihydrate. The resulting solution was stirred
for 10 minutes. To this solution were added, in
portions, 2,268.4 grams of Ag_2O . The resulting sil-
15 ver-containing solution was thereafter stirred for an
additional hour and 453.6 grams of monoethanolamine
were then added to the stirred silver-containing
solution. Stirring was continued for an additional
10 minutes. This solution was then diluted to a
20 total volume of 5,000 ml by addition of distilled
water.

High-purity alpha-alumina support pellets
(1,925.4 grams) having platelet morphology of the
type disclosed in Canadian Patent Appl. Ser. No. 515,864-8,
25 filed August 13, 1986, having a surface area of
about $1.2 \text{ m}^2/\text{g}$ and a porosity of about 0.8 cc/g were
placed in a tube which was then evacuated, following
which a first impregnation was conducted by immersing
the support particles in the first silver-containing
30 impregnation solution formed as described above, for
one hour. Excess impregnation solution was then
drained and the resulting pellets were then belt-
roasted at 500 degrees C in a 66 SCFH air flow for
2.5 minutes. The resulting material contained 24.9
35 percent silver by weight.

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A co-impregnation solution was prepared by placing 1,260.5 grams of ethylenediamine into a 5,000 ml beaker and mixing therewith 1,249.6 grams of distilled water to form a solution. To the stirred solution were slowly added 1,262.4 grams of oxalic acid dihydrate and, with continuous stirring, 2,211.7 grams of silver oxide were slowly added. When dissolution was complete, 442.3 grams of monoethanolamine were added directly to the solution. To the silver-containing solution were added 26.4 grams of potassium nitrate dissolved in 50 milliliters of distilled water. To the resulting solution was added sufficient water to dilute the solution to 4,875 ml. The silver-impregnated catalyst pellets (2,495.6 grams) were impregnated in a manner similar to the first impregnation described above. The resulting catalyst contained 39.8 weight percent silver and 0.098 weight percent potassium.

Example 3 - Sequential Preparation
Of A Potassium Nitrate-Containing
Supported High Silver Concentration Catalyst:

A silver-containing impregnation solution was prepared by dissolving 787.0 grams ethylenediamine with 780.0 grams of distilled water and stirring for a period of 10 minutes. To the stirred solution were slowly added 788.3 grams of oxalic acid dihydrate. The resulting solution was stirred for 10 minutes. To this solution were added, in portions, 1,380.8 grams of Ag_2O . The resulting silver-containing solution was thereafter stirred for an additional hour, following which 276.3 grams of monoethanolamine were added to the stirred silver-containing solution. Stirring was continued for an additional 10 min-

utes. This solution was then diluted to a total volume of 3,125 ml by addition of distilled water.

High-purity alpha-alumina support pellets (1,172.5 grams), having platelet morphology, of the type disclosed in Canadian Patent Appl. Ser. No. 515,864-8, filed August 13, 1986, having a surface area of about $1.2 \text{ m}^2/\text{g}$ and a porosity of about 0.8 cc/g were placed in a tube which was then evacuated, following which the support pellets were impregnated by immersing them in a portion of the impregnating solution formed as described above for one hour. The excess impregnation solution was drained and the resulting pellets were then belt-roasted at 500 degrees C in a 66 SCFH air flow for 2.5 minutes. The resulting material contained 24.3 percent silver, by weight.

A second silver-containing impregnation solution was prepared in a manner similar to the preparation of the silver-containing impregnation solution described above, employing 472.2 grams ethylenediamine, 468.0 grams distilled water, 472.9 grams oxalic acid dihydrate, 828.5 grams silver nitrate, 165.8 grams monoethanolamine, and diluted to a total volume of 18.75 milliliters by addition of distilled water.

High-purity alpha-alumina support pellets (703.5 grams), similar to those employed above, were then impregnated with the solution described immediately above in a manner similar to the first impregnation described above. The resulting material contained 24.6 percent silver.

The two batches of impregnated alpha-alumina formed as described above were then combined.

A second impregnation cycle was performed by impregnating the silver-containing catalyst material of the combined batches with a fresh silver impregna-

tion solution. This solution was prepared in a manner similar to the impregnation solutions used in the first impregnation cycle, employing 1,196.2 grams ethylenediamine, 1,185.6 grams distilled water, 5 1,198.1 oxalic acid dihydrate, 2,098.7 grams silver oxide, 419.9 grams monoethanolamine, and diluted to 4,750 milliliters by addition of distilled water. The silver-containing catalyst material formed in the first impregnation cycle was impregnated with the 10 fresh silver impregnation solution in a manner similar to the manner in which the first impregnation cycle was conducted. The silver-containing catalyst resulting from the second impregnation cycle contained 38.5 weight percent silver.

15 Potassium nitrate was incorporated into the catalyst material by immersing 3,040.6 grams of the silver-impregnated pellets in a solution containing 24.8 grams KNO_3 in 4,000 ml of distilled water. After draining, the material was dried at 120 degrees 20 C for 2 hours to yield a catalyst containing 38.5 percent silver and 0.010 percent potassium, by weight.

The catalysts described above in Examples 2 and 3 may be used in carrying out the process of this 25 invention.

Example 4:

Two grams (2.8 milliliters) of 14/20 mesh catalyst is placed in a stainless steel tubular micro-reactor 10.2 centimeters long and having a 9.52 millimeters outside diameter and a 7.75 millimeters 30 inside diameter. The catalyst comprises 21.7 percent by weight silver and potassium nitrate (1.0 percent potassium) on a high-purity alpha-alumina support 35

having platelet morphology of the type described in Canadian Patent Application Serial No. 515,864-8, filed August 13, 1986. The support has a surface area of about $1.2 \text{ m}^2/\text{g}$, a porosity of about 0.88 cc/g and a
5 leachable sodium content of less than 50 ppm by weight. At a pressure of 25 psig, a GHSV of $1,718 \text{ hr}^{-1}$ and a reactor temperature of 255 degrees C, a feedstream comprising a mixture of 9.70 percent by volume propylene, 8.10 percent by volume oxygen, 230
10 ppm by volume ethyl chloride, 230 ppm by volume nitric oxide, 2.6 percent by volume methane and the balance nitrogen is fed to the reactor. Propylene oxide is produced.

Carbon dioxide is added to the feedstream and
15 the nitrogen level reduced so that the feed gas contains 9.99 volume percent propylene, 7.94 volume percent oxygen, 6.84 volume percent carbon dioxide, 230 ppm by volume nitric oxide, 230 ppm by volume ethyl chloride, 2.6 volume percent methane and the
20 balance nitrogen ballast gas. All other conditions are maintained the same. Propylene oxide is produced under these conditions.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An improved process for the epoxidation of alkene selected from the group consisting of cyclic and acyclic alkenes containing up to about 12 carbon atoms to form the corresponding alkene oxide wherein:

(a) said alkene is contacted with oxygen-containing gas under epoxidation conditions in a reaction zone in the presence of (i) a performance-enhancing gaseous organic halide compound, (ii) at least one gaseous efficiency-enhancing member of a redox-half reaction pair selected from compounds containing oxygen in combined form with a polyvalent element, (iii) a supported silver catalyst, comprising a catalytically effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt selected from the group consisting of salts of oxyanions of polyvalent elements on a support, said oxyanion of said efficiency-enhancing salt and said gaseous efficiency-enhancing member (ii) containing a common polyvalent element and either belonging to the same redox-half reaction pair or belonging to different half reaction pairs in a series of chemically-related half reaction equations, to produce the corresponding alkene oxide, carbon dioxide and water;

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(b) a reactor effluent comprising said alkene oxide, carbon dioxide, and unreacted alkene is withdrawn from said reaction zone;

(c) at least a portion of the alkene oxide contained in said reactor effluent is removed; and in which

(d) a recycle stream comprising at least a portion of said reactor effluent from which the alkene oxide has been removed is recycled to said reaction zone;

the improvement which comprises removing an effective amount of carbon dioxide from the recycle stream prior to said recycle stream being introduced into said reaction zone to diminish the activity-reducing effect of carbon dioxide upon the said supported silver catalyst.

2. An improved process for the epoxidation of ethylene to form the corresponding ethylene oxide wherein:

(a) said ethylene is contacted with oxygen-containing gas under epoxidation conditions in a reaction zone in the presence of (i) a performance-enhancing gaseous organic halide compound, (ii) at least one gaseous efficiency-enhancing member of a redox-half reaction pair selected from compounds containing oxygen in combined form with a polyvalent element, (iii) a

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supported silver catalyst, comprising a catalytically effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt selected from the group consisting of salts of oxyanions of polyvalent elements on a support, said oxyanion of said efficiency-enhancing salt and said gaseous efficiency-enhancing member (ii) containing a common polyvalent element and either belonging to the same redox-half reaction pair or belonging to different half reaction pairs in a series of chemically-related half reaction equations, to produce the corresponding ethylene oxide, carbon dioxide and water;

(b) a reactor effluent comprising said ethylene oxide, carbon dioxide, and unreacted ethylene is withdrawn from said reaction zone;

(c) at least a portion of the ethylene oxide contained in said reactor effluent is removed; and in which

(d) a recycle stream comprising at least a portion of said reactor effluent from which the ethylene oxide has been removed is recycled to said reaction zone;

the improvement which comprises removing an effective amount of carbon dioxide from the recycle stream prior to said recycle stream being introduced into said reaction zone to diminish the activity-reducing effect of carbon dioxide upon the said supported silver catalyst.

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3. An improved process for the epoxidation of propylene to form the corresponding propylene oxide wherein:

(a) said propylene is contacted with oxygen-containing gas under epoxidation conditions in a reaction zone in the presence of (i) a performance-enhancing gaseous organic halide compound, (ii) at least one gaseous efficiency-enhancing member of a redox-half reaction pair selected from compounds containing oxygen in combined form with a polyvalent element, (iii) a supported silver catalyst, comprising a catalytically effective amount of silver and an efficiency-enhancing amount of at least one efficiency-enhancing salt selected from the group consisting of salts of oxyanions of polyvalent elements on a support, said oxyanion of said efficiency-enhancing salt and said gaseous efficiency-enhancing member (ii) containing a common polyvalent element and either belonging to the same redox-half reaction pair or belonging to different half reaction pairs in a series of chemically-related half reaction equations, to produce the corresponding propylene oxide, carbon dioxide and water;

(b) a reactor effluent comprising said propylene oxide, carbon dioxide, and unreacted propylene is withdrawn from said reaction zone;

(c) at least a portion of the propylene oxide contained in said reactor effluent is removed; and in which

(d) a recycle stream comprising at least a portion of said reactor effluent from which the propylene oxide has been removed is recycled to said reaction zone;

the improvement which comprises removing an effective amount of carbon dioxide from the recycle stream prior to said recycle stream being introduced into said reaction zone to diminish the activity-reducing effect of carbon dioxide upon the said supported silver catalyst.

4. The process of claim 1, 2 or 3 wherein said gaseous efficiency-enhancing member of a redox-half reaction pair and said efficiency-enhancing salt of a member of a redox-half reaction pair comprise members of the same redox-half reaction pair.

5. The process of claim 1, 2 or 3 wherein said at least one gaseous efficiency-enhancing member of a redox-half reaction pair comprises nitric oxide, nitrogen dioxide, N_2O_3 , N_2O_4 , a gas capable of generating at least one of nitric oxide and nitrogen dioxide under epoxidation conditions, or mixtures thereof.

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6. the process of claim 1, 2 or 3 wherein said at least one gaseous efficiency-enhancing member of a redox-half reaction pair comprises nitric oxide, nitrogen dioxide, or mixtures thereof.

7. The process of claim 1, 2 or 3 wherein said at least one efficiency-enhancing salt of a member of a redox-half reaction pair comprises potassium nitrate.

8. The process of claim 2 wherein said efficiency-enhancing salt is present in said catalyst in an amount such that the cation of said salt comprises from about 0.01 to about 2.0 percent by weight, based on the total weight of said catalyst.

9. The process of claim 3 wherein said efficiency-enhancing salt is present in said catalyst in an amount such that the cation of said salt comprises from about 0.01 to about 5 percent by weight, based on the total weight of said catalyst.

10. The process of claim 2 wherein the concentration of carbon dioxide entering said reaction zone is maintained at or below 3 volume percent.

11. The process of claim 3 wherein the concentration of carbon dioxide entering said reaction zone is maintained at or below 10 volume percent.

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12. The process of claim 1, 2 or 3 wherein a performance-enhancing gaseous halide comprising 1, 2-dichloroethane, ethyl chloride, or mixtures thereof is present in the reaction zone.

13. The process of claim 1, 2 or 3 wherein said catalyst contains from about 8 to about 50 percent silver by weight.

14. The process of claim 1, 2 or 2 wherein said catalyst is provided in a fixed bed reactor.

15. The process of claim 1, 2 or 3 wherein said catalyst is provided in a fluidized bed reactor.

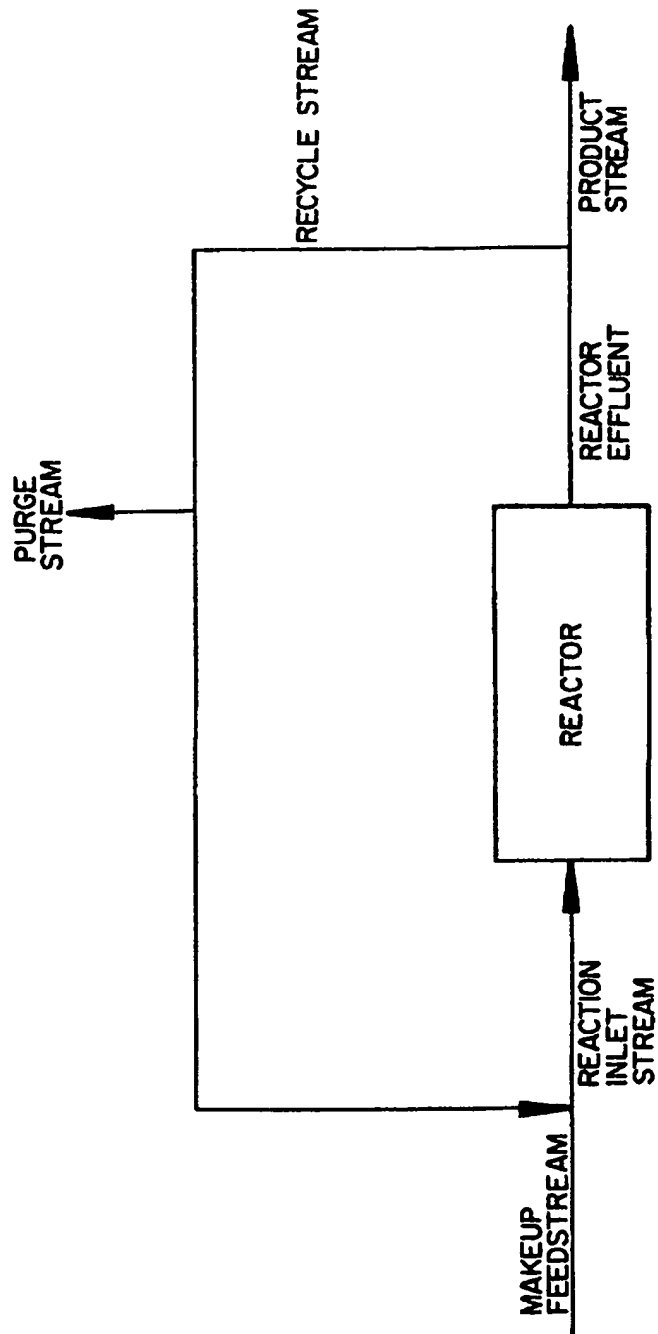
16. The process of claim 1, 2 or 3 wherein said gaseous efficiency-enhancing member of a redox-half reaction pair further comprises one or more of phosphine, carbon monoxide, sulfur dioxide, and sulfur trioxide.

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W. G. Hopby



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